

Resonant Elastic X-Ray Scattering in Graphite and Diamond

Y. Muramatsu¹, M. M. Grush² and R. C. C. Perera²

¹ NTT Integrated Information & Energy Systems Laboratories, Musashino, Tokyo 180-8585, Japan

² Lawrence Berkeley National Laboratory, Berkeley, California 94720, USA

INTRODUCTION

Resonant soft x-ray emission spectroscopy, using highly brilliant monochromatized synchrotron radiation as excitation probes, has become an exciting focus of current spectroscopic methods for materials science, because it can provide a new experimental way to analyze the electronic structure of materials in relation to the band structure [1]. Resonant radiative-decay can generally be categorized into two processes: One is resonant inelastic x-ray scattering (RIXS) caused by the correlation of the “spectator” electrons, excited in threshold localized states, with valence electrons, and the other is resonant elastic x-ray scattering (REXS) caused by the radiative transition of the “participator” electrons to the inner core-holes. The “spectator” RIXS has been intensively studied by many researchers, and interesting phenomena concerning the radiative-decay process have been observed in many materials [2, 3]. On the other hand, the study of the “participator” REXS is less advanced: intense REXS has been observed only in boron compounds [4-6]. However, we believe that participator REXS should be observed in other compounds and it should also provide significant information about the radiative-decay process and electronic structure. We first focused on graphite and diamond because the electronic structures and RIXS of these typical carbon materials have already been well investigated. In this paper, we demonstrate the energy spectra of elastic x-ray scattering of graphite and diamond at the C *K* threshold and discuss REXS in carbon materials in relation to the electronic structure characterized by sp²- and sp³-carbon atoms.

EXPERIMENT

Commercially obtained powder samples of graphite and diamond were used for the REXS measurements. The average particle size of the graphite powder was 45 μm and that of the diamond powder was 36 μm. X-ray scattering and x-ray emission spectra were measured using a grating x-ray spectrometer with a position sensitive detector (PSD) installed in beamline BL-8.0. Fluorescence yield (FY) absorption spectra were also measured using this spectrometer. Energy spectra of elastic x-ray scattering were measured by varying the window width of the PSD in the FY-absorption measurements. Total-electron-yield (TEY) absorption spectra were measured by monitoring the sample photocurrent in BL-6.3.2.

RESULTS AND DISCUSSION

Figure 1 shows the elastic x-ray scattering spectra of (a) graphite and (b) diamond powders. The upper panels show the C *K* x-ray emission spectra of graphite and diamond, observed with the PSD in the grating x-ray spectrometer in BL-8.0. In these measurements, the PSD was aligned to detect x-rays from 263 to 298 eV. Elastic x-ray scattering should be observed in the energy region above 283 eV, and RIXS or fluorescent x-ray emission should be observed below 284 eV. To distinguish the elastic x-ray scattering from RIXS, we measured FY-absorption spectra by varying the window width of the PSD. We could detect RIXS in (B) the narrow window of 263–283 eV and could detect both RIXS and elastic x-ray scattering in (A) the wide window of 263–298 eV. Thus, we could obtain the energy spectra of the elastic x-ray scattering by subtracting the FY-absorption spectrum obtained with the narrow window from that obtained with the wide window, (A) - (B), as shown in the lower panels. In the elastic x-ray spectra of the graphite, an intense peak was observed near 284 eV and small bumps were observed in the

energy region from 285–292 eV. In diamond, few significant peaks, except for a small peak at 288 eV, were observed in the elastic x-ray scattering spectrum.

Figure 2 shows the elastic x-ray scattering spectra of graphite and diamond superimposed on the individual TEY-absorption spectra. In graphite, the intense 284-eV peak approximately corresponds to the π^* -absorption peak and the broad bumps in the range from 285–292 eV correspond to the region between the π^* - and σ^* -absorption peaks. No significant scattering structure was observed above the σ^* -peak region. Therefore, this elastic x-ray scattering in graphite corresponds to the threshold unoccupied electronic structure of $p\pi^*$ states in sp^2 -carbon atoms and it should be attributed to REXS. This REXS transition via $p\pi^*$ states agrees with the intense REXS observed in trigonally coordinated boron compounds [4, 5]. In diamond, the small peak at 288 eV corresponds to the threshold peak due to an exciton in the TEY-absorption. This small scattering peak may also be REXS via exciton states, which was also explained with the vibronic coupling effects of core excitons by Ma et al. [7]. However, this REXS in diamond is negligible compared with that in graphite. This agrees with the above-mentioned REXS mechanism, because there are no $p\pi^*$ states in the sp^3 -carbon atoms of diamond. This means that we may experimentally distinguish the $p\pi^*$ states from the complicated hybridized-electronic-structure in unoccupied states of carbon compounds by using REXS spectroscopy.

Figure 3 shows the FY-absorption spectra of graphite taken with the wide and narrow windows, superimposed on each other by normalizing the x-ray scattering intensities. The spectral height at 284 eV in the narrow-window absorption spectra shows the probability of the spectator RIXS process, and that in the wide-window absorption shows the sum of the spectator RIXS and participator REXS. We can therefore quantitatively determine the transition probability ratio between the spectator RIXS and participator REXS by comparing these peak heights. From the figure, the transition probabilities of the spectator RIXS and participator REXS in graphite can be determined to be 66% and 34%, respectively.

CONCLUSION

REXS was observed at the C K threshold of graphite. It is caused by the transition of the participator electrons via $p\pi^*$ states in sp^2 -carbon atoms. This shows that REXS spectroscopy can identify the $p\pi^*$ orbitals in the unoccupied hybridized orbitals of carbon atoms. The transition probability ratio between participator REXS and spectator RIXS in the resonant radiative-decay process can be determined from REXS spectroscopy, confirming that REXS at thresholds provides significant information about the radiative-decay process and about the electronic structures of materials.

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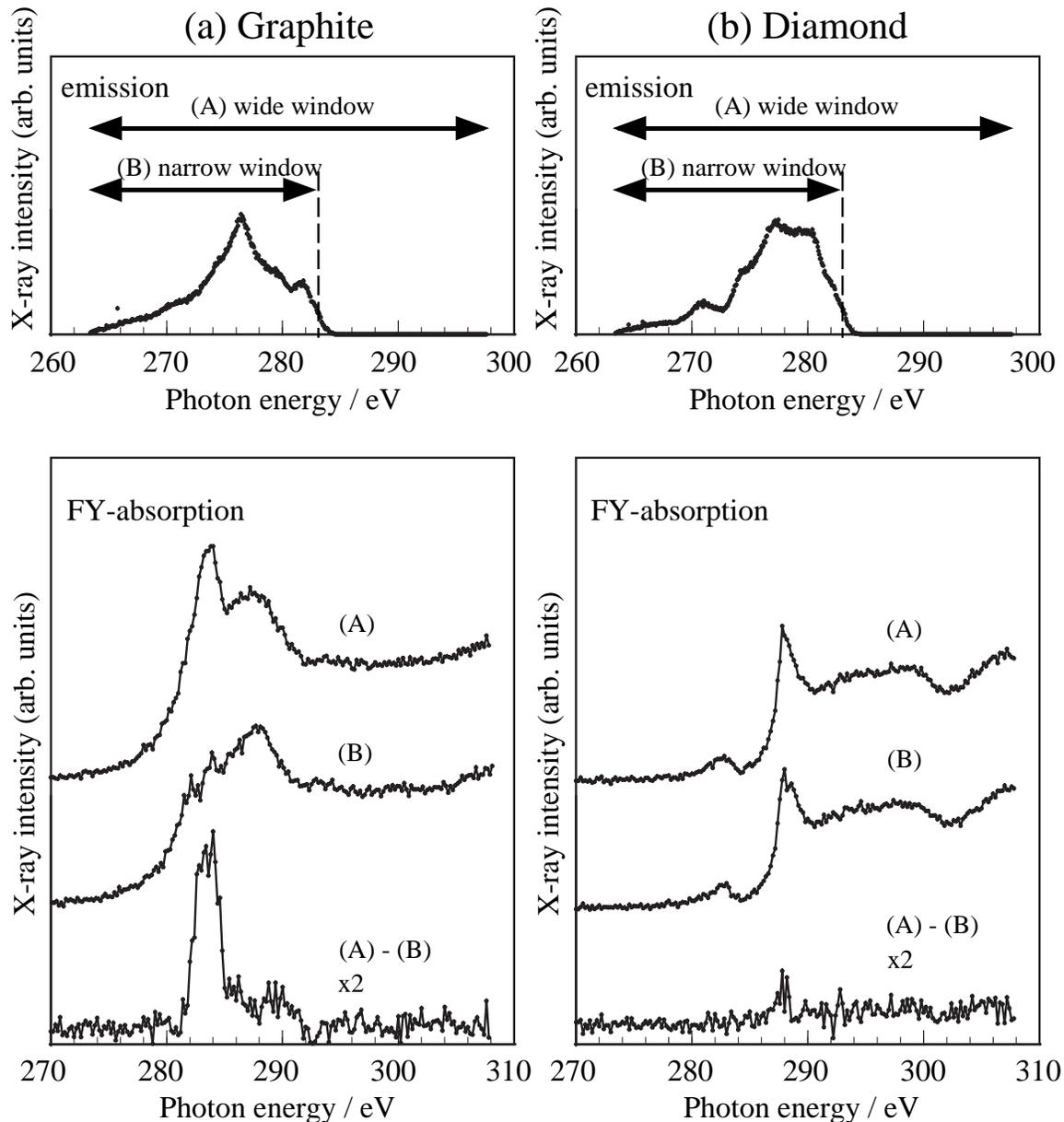


Figure 1 Upper panels show the C K x-ray emission spectra of (a) graphite and (b) diamond. Lower panels show the fluorescence-yield (FY) absorption spectra taken with (A) wide and (B) narrow windows, and the subtracted spectra of (A) - (B). The subtracted spectra give elastic x-ray scattering spectra at the threshold.

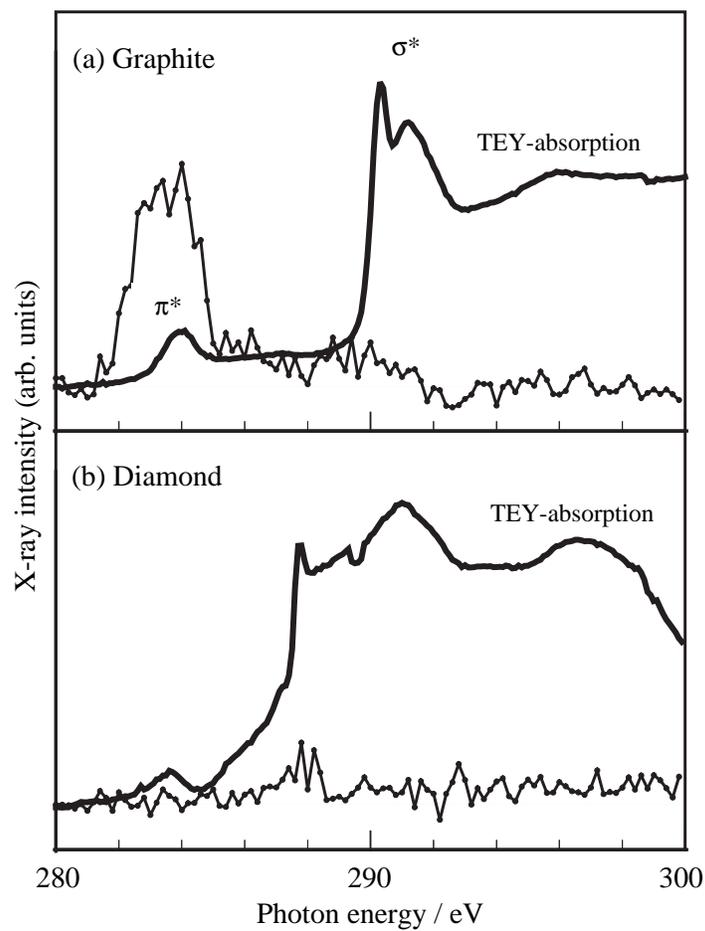


Figure 2 Elastic x-ray scattering spectra of (a) graphite and (b) diamond, superimposed on total-electron-yield (TEY) absorption spectra.

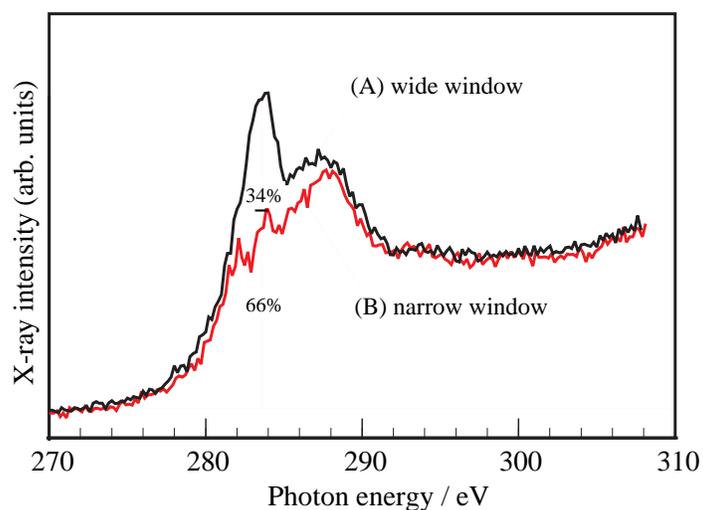


Figure 3 FY-absorption spectra of graphite taken with (A) wide and (B) narrow windows.

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Principal investigator: Yasuji MURAMATSU, NTT Integrated Information & Energy Systems Laboratories,
 Email: murama@ilab.ntt.co.jp Telephone: +81-422-59-2521